

AD-A265 509



2

## OFFICE OF NAVAL RESEARCH/DARPA

### Publications

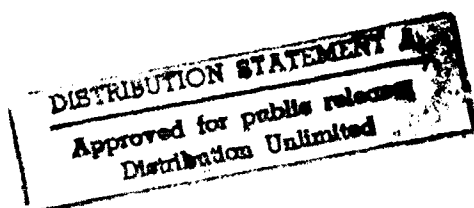
for

Contract #: N00014-89-J-1961  
R&T Code 4132039---01

### **COMPOSITE MATERIALS WITH IMPROVED PROPERTIES IN COMPRESSION**

Professor William P. Weber  
Loker Hydrocarbon Research Institute  
Department of Chemistry  
University of Southern California  
Los Angeles, CA 90089-1661

Reproduction in whole, or in part, is permitted for any purposes  
by the United States Government



DTIC  
SELECTE  
JUN 08 1993  
S B D

93 6 04 013

93-12587



## ABSTRACT DISTRIBUTION LIST

Dr. John J. Aklonis  
Department of Chemistry  
University of Southern California  
Los Angeles, CA 90089

Dr. James Economy  
Materials Science & Engineering Dept.  
University of Illinois  
Urbana, IL 61820-6219

Dr. Jerry I. Scheinbeim  
Department of Mechanical and  
Materials Science  
Rutgers University  
Piscataway, NJ 08854

Dr. William P. Weber  
Department of Chemistry  
University of Southern California  
Los Angeles, CA 90089-1661

DTIC QUALITY INSPECTED 2

Accession For	
NTIS Grant	<input checked="" type="checkbox"/>
NTIS Rep	<input type="checkbox"/>
Unpublished	<input type="checkbox"/>
Justification	
For	
Distribution/	
Availability Index	
Avail. and/or	
Dist	Serial
A-1	

## TECHNICAL REPORT DISTRIBUTION LIST

Dr. Ronald A. De Marco (2)  
Director, Chemistry Division  
Code 1113  
Office of Naval Research  
800 North Quincy Street  
Arlington, VA 22217-5000

Dr. Richard W. Drisko (1)  
Naval Civil Engineering Laboratory  
Code L52  
Port Hueneme, CA 93043

Dr. James S. Murday (1)  
Chemistry Division, Code 6100  
Naval Research Laboratory  
Washington, DC 20375-5000

Dr. Harold H. Singerman (1)  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. Robert Green (1)  
Director, Chemistry Division  
Code 385  
Naval Air Weapons Center  
Weapons Division  
China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1)  
Code 2840  
Naval Surface Warfare Center  
Carderock Division Detachment  
Annapolis, MD 21402-1198

Dr. Elek Lindner (1)  
Naval Command  
Control & Ocean Surveillance Center  
RDT&E Division  
San Diego, CA 92152-5000

Defense Technical Information Center (2)  
Building 5, Cameron Station  
Alexandria, VA 22314

Dr. Bernard E. Douda (1)  
Crane Division  
Naval Surface Warfare Center  
Crane, IN 47522-5000

Dr. Kenneth J. Wynne (1)  
Program Manager  
Organic & Polymeric Materials  
Office of Naval Research  
Arlington, VA 22217-5000

Dr. Richard Loda (2)  
Defense Sciences Office  
Defense Adv. Research Projects Agency  
3701 North Fairfax Drive  
Arlington, VA 22203-1714

Dr. JoAnn Milliken (1)  
Scientific Officer  
Polymer and Organic Chemistry  
Office of Naval Research  
Arlington, VA 22217-5000

Number of copies forwarded.

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>2. Reducing burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993	3. REPORT TYPE AND DATES COVERED Journal Article	
4. TITLE AND SUBTITLE Partial and complete chemical modification of poly(1,1-dimethyl-1-sila- <u>cis</u> -pent-3-ene) by addition of dichloroketene			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) H.S.J. Lee and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer</u> , <u>33</u> , 1748 (1992).				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS chemical modification poly(1,1-dimethyl-1-sila- <u>cis</u> -pent-3-ene) dichloroketene			15. NUMBER OF PAGES 8	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

# Partial and complete chemical modification of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) by addition of dichloroketene

Howard Shih Jen Lee and William P. Weber\*

K. B. and D. P. Loker Hydrocarbon Research Institute, Department of Chemistry,  
University of Southern California, Los Angeles, CA 90089-1661, USA

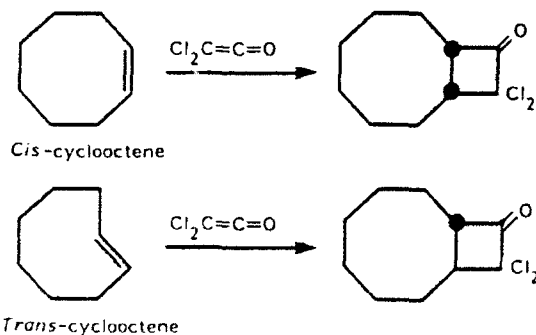
(Received 12 December 1990; accepted 8 March 1991)

Dichloroketene, generated by the ultrasound-promoted dechlorination of trichloroacetyl chloride with zinc, has been added to the carbon-carbon double bonds of poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (poly-I). The molecular-weight distribution of the adduct polymer in which all of the carbon-carbon double bonds have reacted with dichloroketene, poly[2,2-dichloro-*cis*-3,4-bis(methylene)cyclobutanone dimethylsilylene], 100% poly(I-Cl<sub>2</sub>C=C=O), has been characterized by gel permeation chromatography. The microstructure of 100% poly(I-Cl<sub>2</sub>C=C=O) has been elucidated by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si nuclear magnetic resonance as well as by infra-red spectroscopy. Similarly, a series of random copolymers have been prepared in which only some of the carbon-carbon double bonds of poly-I have reacted with dichloroketene. These have been characterized as above. The glass transition temperatures (*T*<sub>g</sub>) of these copolymers, as well as that of 100% poly(I-Cl<sub>2</sub>C=C=O), have been determined by differential scanning calorimetry. The *T*<sub>g</sub> values are found to increase linearly with the percentage of the carbon-carbon double bonds of poly-I that have reacted with dichloroketene.

(Keywords: dichloroketene; addition; *T*<sub>g</sub> values; copolymers)

## INTRODUCTION

Dichloroketene (II) is well known to undergo cycloaddition reactions with the C-C double bonds of alkenes<sup>1</sup>. These [2 + 2] cycloaddition reactions proceed stereospecifically via a concerted [ $\pi_2^2 + \pi_2^2$ ] reaction in which the  $\pi$ -system of the alkene and the C-C double bond of the ketene approach each other via an orthogonal trajectory<sup>2</sup>. These reactions yield 2,2-dichloro-3,4-disubstituted cyclobutanones in which the geometrical relationship of the substituents is identical to that in the starting alkene, i.e. *cis*-alkenes yield *cis*-cyclobutanones and *trans*-alkenes yield *trans*-cyclobutanones.



Unlike less reactive ketenes, II reacts even at room temperature with the C-C double bonds of unactivated alkenes, such as cyclopentene and cyclohexene<sup>3</sup>. Even with 1,3-dienes, which might react with II via a [2 + 4] pathway, [2 + 2] cycloaddition products (2,2-dichloro-

3-vinylcyclobutanones) are obtained<sup>4-6</sup>. For example, [2 + 2] cycloaddition reaction of II with one of the C-C double bonds of 5-trimethylsilylcyclopentadiene yields 7,7-dichloro-4-*exo*-trimethylsilylbicyclo[3.2.0]hept-2-en-6-one<sup>7,8</sup>. Despite considerable interest in the reactions of allylic silanes<sup>9</sup>, this is the only case of such a reaction.

The facile generation of II under mild experimental conditions from inexpensive readily available starting materials recommends this reaction. II can be generated either by the homogeneous dehydrohalogenation of dichloroacetyl chloride with triethylamine or by the heterogeneous dechlorination of trichloroacetyl chloride with active zinc<sup>10</sup>. The recent observation that ultrasound promotes this heterogeneous reaction further facilitates the preparation of 2,2-dichlorocyclobutanones<sup>11</sup>.

2,2-Dichlorocyclobutanones are themselves versatile synthetic intermediates. For example, they can easily be converted to cyclobutanones by the dissolving metal reduction of the C-Cl bonds<sup>12</sup>. This transformation can also be achieved by reaction with tri-*n*-butyltin hydride<sup>12</sup>. They can likewise be modified under basic conditions to yield  $\alpha$ -alkoxycyclopropane carboxylic acids via a Favorskii-type ring contraction reaction<sup>13-15</sup>.

Despite the high reactivity of II discussed above, no examples of its reactions with C-C double bonds of unsaturated polymers such as *cis*-1,4-polybutadiene have been reported. This is surprising since there is considerable interest in the chemical modification of polymers<sup>16-19</sup>. Modification of functional groups in a polymer is one of the general routes for the synthesis of new polymeric materials. Many such reactions lead

\*To whom correspondence should be addressed

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>2. Reducing the burden of the collection of information is a primary goal of the Department of Defense. It is the policy of the Department to review and, if necessary, to eliminate or reduce the burden of the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article
4. TITLE AND SUBTITLE Addition of difluorocarbene to poly(1-methyl-1-phenyl-1-sila-cis-pent-3-ene). Thermal stability and characterization of microstructures by $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ and $^{29}\text{Si}$ NMR spectroscopy.				5. FUNDING NUMBERS N00014-89-J-1961
6. AUTHOR(S) H.S.J. Lee and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062				8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217				10. SPONSORING / MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES Published in <u>Polymer</u> , <u>33</u> , 4299 (1992).				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited				12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS chemical modification of polymers addition difluorocarbene thermal stability				15. NUMBER OF PAGES 5
				16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

# Addition of difluorocarbene to poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene). Thermal stability and characterization of microstructures by $^1\text{H}$ , $^{13}\text{C}$ , $^{19}\text{F}$ and $^{29}\text{Si}$ n.m.r. spectroscopy

Howard Shih-Jen Lee and William P. Weber\*

K. B. and D. P. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA  
(Received 15 March 1991, accepted 24 June 1991)

Excess difluorocarbene, generated by the sodium iodide catalysed decomposition of (trifluoromethyl)phenylmercury, adds in a stereospecific *cis* manner to the carbon-carbon double bonds of poly(1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) (I) to yield poly(3,4-difluoromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) ( $\text{F}_2\text{C-I}$ ). Similarly, a series of random copolymers has been prepared in which only some of the carbon-carbon double bonds of I have reacted with difluorocarbene. The microstructures of these difluorocyclopropanated polymers have been determined by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  n.m.r. spectroscopy. The glass transition temperatures of these copolymers are found to depend on the extent of difluorocyclopropanation. The thermal stability of  $\text{F}_2\text{C-I}$  has been determined by thermogravimetric analysis. The thermal stability of I,  $\text{F}_2\text{C-I}$ , poly(3,4-dichloromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene) ( $\text{Cl}_2\text{C-I}$ ) and (1-methyl-3,4-methylene-1-phenyl-1-sila-*cis*-pent-3-ene) ( $\text{H}_2\text{C-I}$ ) are compared.

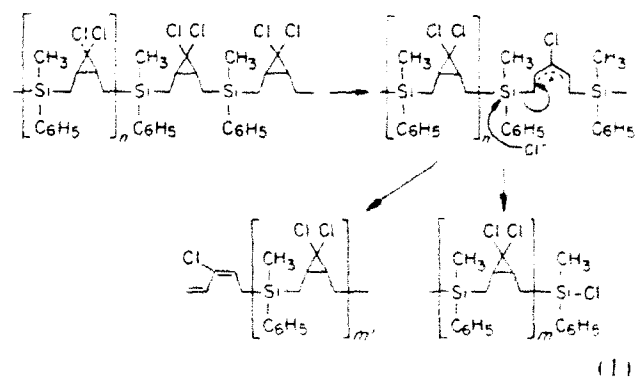
(Keywords: difluorocarbene; copolymers; microstructure)

## INTRODUCTION

There is considerable interest in the chemical modification of polymers<sup>1-4</sup>. Such reactions permit the preparation of polymers which cannot be prepared by monomer polymerization. In addition, partial chemical modification permits the synthesis of novel copolymers. Carbene addition to unsaturated polymers is one method for facile derivatization. For example, dichloro- and difluorocarbene add stereospecifically to the carbon-carbon double bonds of *cis*- and *trans*-1,4-polybutadiene<sup>5-9</sup>.

We have previously added dichlorocarbene to the carbon-carbon double bonds of I and found the polymer  $\text{Cl}_2\text{C-I}$  to undergo facile chain scission at low temperature (95°C)<sup>10</sup>. This degradation process probably occurs by a two-step mechanism. The first involves ionization of one of the carbon-chlorine bonds with concerted disrotatory opening of the cyclopropane ring to yield an allylic cation. This symmetry-allowed process is accelerated due to stabilization of the allylic cation by the two adjacent methylphenylsilyl groups. It is well known that silicon has a profound stabilizing effect on  $\beta$ -carbocation centres<sup>11</sup>. Subsequent nucleophilic attack by the chloride anion on an adjacent methylphenylsilyl centre results in scission of the polymer chain (equation (1)).  $\text{F}_2\text{C-I}$  is expected to be more stable than  $\text{Cl}_2\text{C-I}$  if the first step in this process is rate determining since ionization of a carbon-fluorine bond will occur less

readily than that of a carbon-chlorine bond<sup>12</sup>. On the other hand, if nucleophilic attack on one of the methylphenylsilyl centres that is  $\beta$  to the allylic carbocation is rate limiting, then we might anticipate that the difluorocarbene adduct polymer would decompose more rapidly since a silicon-fluorine bond is much stronger than a silicon-chlorine bond<sup>13</sup>.



A series of copolymers composed of 1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene (II) and 3,4-difluoromethylene-1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene (III) units has been prepared by controlling the extent of the difluorocyclopropanation of the carbon-carbon double bonds of I, in the hope that these will have predictable physical properties between those of I and  $\text{F}_2\text{C-I}$ .

\*To whom correspondence should be addressed

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article	
4. TITLE AND SUBTITLE Dimerization and polymerization of 2,3-benzo-5-silaspiro-[4.4]nona-2,7-diene.				5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) L. Wang, Y-H. Ko and W.P. Weber					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Macromolecules</u> , <u>25</u> , 2828 (1992).					
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  See attachments					
14. SUBJECT TERMS Dimerization Polymerization Anionic ROMP				2,3-benzo-5-silaspiro[4.4]nona-2,7-diene	
				15. NUMBER OF PAGES 4	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited		



# Dimerization and Polymerization of 2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene

Liming Wang, Young-Hoon Ko, and William P. Weber\*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received October 21, 1991; Revised Manuscript Received January 24, 1992

**ABSTRACT:** Treatment of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I) with catalytic amounts of *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF results in dimerization of I to give 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II). On the other hand, ring-opening metathesis polymerization (ROMP) of I cocatalyzed by tungsten hexachloride and tetraphenyltin gives poly[(3,4-benzo-1-silacyclopent-3-en-1-ylene)-*cis*- and -*trans*-but-2-en-1,4-ylene] (*cis*- and *trans*-III).

## Introduction

We have been interested in the ring-opening polymerization of 1-silacyclopent-3-enes. These reactions generally lead to poly(1-sila-*cis*-pent-3-enes).<sup>1</sup> Recently, we studied the anionic polymerization of several 5-silaspiro[4.4]nona-2,7-diene systems and found that dimerization competes with polymerization in some of these cases.<sup>2,3</sup> In an attempt to better understand the factors controlling this competition, we studied both the anionic and ring-opening metathesis polymerization of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I).

## Results and Discussion

2,3-Benzo-5-silaspiro[4.4]nona-2,7-diene (I) was prepared from benzyl(chloromethyl)dichlorosilane (IV) (Figure 1). Thus aluminum chloride catalyzed intramolecular Friedel-Crafts cyclization of IV gives 1,1-dichloro-3,4-benzo-1-silacyclopent-3-ene (V),<sup>4</sup> which reacts with 1,3-butadiene and magnesium in THF to yield I.

Treatment of I with catalytic amounts of *n*-butyllithium and HMPA did not result in anionic ring-opening polymerization and formation of poly[(3,4-benzo-1-silacyclopent-3-en-1-ylene)-*cis*-but-2-en-1,4-ylene] (*cis*-III) but rather in formation of a dimer 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II) (Figure 2). By comparison, both 1,1-dimethyl-1-silacyclopent-3-ene and 1,1-dimethyl-3,4-benzo-1-silacyclopentene undergo anionic ring-opening polymerization to yield respectively poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene)<sup>1</sup> and poly(1,1-dimethyl-3,4-benzo-1-silapentene).<sup>5</sup>

The anionic dimerization of I to yield II may be related to the dimerization of 2,3-dimethyl-5-silaspiro[4.4]nona-2,7-diene (VI) which gives 2,3:12,13-tetramethyl-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (VII), whose structure has been rigorously established by X-ray crystallography.<sup>3</sup> The molecular weight of II was determined by mass spectrometry while its structure was established by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR as well as by IR and UV spectroscopy. In particular, the <sup>29</sup>Si NMR resonance for I is found at 33.51 ppm while that for II is observed at 19.12 ppm, an upfield shift of 14.4 ppm. This is similar to the 13.7 ppm upfield shift that is observed when the <sup>29</sup>Si NMR resonance for VI (25.54 ppm) is compared to that of VII (11.87 ppm). In addition, the chemical shifts of the vinyl protons and carbons are consistent with structure II. In particular, the vinyl protons of I are observed at 6.08 ppm while those for II are found at 5.39 ppm. By comparison, the <sup>1</sup>H NMR signals for the vinyl protons of VI are found at 5.91 ppm while those of VII are

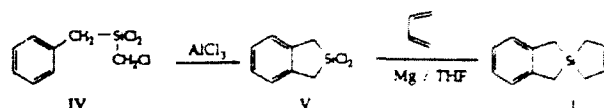


Figure 1. Synthesis of 2,3-benzo-5-silaspiro[4.4]nona-2,7-diene (I).

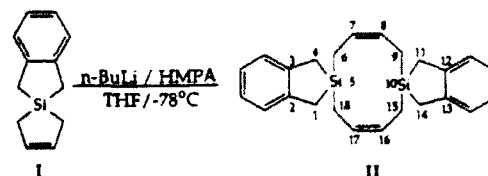


Figure 2. Treatment of I with *n*-butyllithium. Synthesis of 2,3:12,13-dibenzo-5,10-disiladispiro[4.4.4.4]octadeca-2,7,12,16-tetraene (II).

observed at 5.30 ppm. Likewise, the allyl, benzyl and vinyl <sup>13</sup>C NMR signals of I and II can be compared to those of VI and VII (Table I). The nature of the factors which favor dimerization of I and VI under anionic catalysis is not fully understood.

On the other hand, ring-opening metathesis polymerization of I cocatalyzed by tungsten hexachloride and tetraphenyltin with activation by cyclopentene is successful and results in *cis*- and *trans*-III (Figure 3). Ring-opening metathesis polymerization reactions are often stereoselective but not stereospecific.<sup>6</sup> Tungsten hexachloride and tetraphenyltin have been frequently utilized as catalysts for ROMP. Cyclopentene has been previously utilized to activate such ROMP catalyst systems.<sup>7</sup>

The stereochemical composition of III can be determined by integration of the allyl and vinyl hydrogen resonances. Specifically the <sup>1</sup>H NMR signal at 1.94 ppm is assigned to the allylic hydrogens of *trans*-III units, while the resonance at 1.97 ppm is assigned to *cis*-III units. Likewise, the <sup>1</sup>H NMR signal at 5.20 ppm is assigned to the vinyl hydrogens of *trans*-III units while that at 5.25 ppm results from the *cis*-III units. Integration of these is consistent with a polymer composed of 16% *trans*-III units and 84% *cis*-III units.

The <sup>13</sup>C and <sup>29</sup>Si NMR of the 3,4-benzo-1-silacyclopent-3-en-1-ylene (VIII) units are sensitive to microenvironment (Figure 4). Three <sup>29</sup>Si NMR signals are observed. These can be accounted for on the basis that the but-2-en-1,4-ylene (IX) units on either side of VIII units can be both *cis*-IX, one *cis*-IX and one *trans*-IX, or both *trans*-IX. The microenvironment for VIII with *cis*-IX on either side is most probable while that with *trans*-IX units on either side is least probable. The <sup>29</sup>Si NMR

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including its burden, Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article
4. TITLE AND SUBTITLE Anionic dimerization and ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) S.J. Sargeant, S.Q. Zhou, G. Manuel and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  Published in <u>Macromolecules</u> , <u>25</u> , 2832 (1992).				
12a. DISTRIBUTION AVAILABILITY STATEMENT  Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  See attachments				
14. SUBJECT TERMS Anionic dimerization Ring opening polymerization 1,1-divinyl-1-silacyclopent-3-ene			15. NUMBER OF PAGES 5	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

## Anionic Dimerization and Ring-Opening Polymerization of 1,1-Divinyl-1-silacyclopent-3-ene

Steven J. Sargeant, Stephen Q. Zhou, Georges Manuel, and William P. Weber\*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received November 18, 1991; Revised Manuscript Received January 28, 1992

**ABSTRACT:** Anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene (1) cocatalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature ( $-78^{\circ}\text{C}$ ) leads to a mixture of 1,1,6,6-tetravinyl-1,6-disilacyclodeca-3,8-diene (dimer) and poly(1,1-divinyl-1-sila-*cis*-pent-3-ene) (polymer). These have been separated and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR, IR, and UV spectroscopy and elemental analysis. The molecular weight of the dimer has been determined by mass spectroscopy, while the molecular weight distribution of the polymer has been measured by gel permeation chromatography (GPC). Thermogravimetric analysis (TGA) of the polymer in nitrogen gave a 62% char yield. The glass transition temperature ( $T_g$ )  $-65^{\circ}\text{C}$  of the polymer was determined by differential scanning calorimetry (DSC). The mechanism of this reaction has been studied.

## Introduction

The proposal by Yajima that poly(1-methyl-1-silaethane)  $[\text{CH}_3\text{SiHCH}_2]_n$  is a key intermediate in the conversion of poly(dimethylsilane) into  $\beta$  silicon carbide has stimulated considerable interest in the chemistry of polycarbosilanes.<sup>1</sup> Saturated polycarbosilanes such as poly(1,1-dimethyl-1-silabutane) and poly(1,1-dimethyl-1-silaethane) have been prepared by anionic,<sup>2-4</sup> platinum-catalyzed,<sup>5</sup> and thermal<sup>6-9</sup> ring-opening polymerization of 1,1-dimethyl-1-silacyclobutane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane, respectively. We have been interested in the preparation of stereoregular unsaturated polycarbosilane such as poly(1-sila-*cis*-pent-3-ene).<sup>10-12</sup> These have been prepared by the anionic ring-opening polymerization of 1-silacyclopent-3-ene. Studies designed to elucidate the mechanism of these polymerization reactions have shown a number of unusual features. For example, 1,1,3,4-tetramethyl-1-silacyclopent-3-ene undergoes exchange of alkyl groups bonded to silicon rather than polymerization on treatment with *n*-butyllithium and hexamethylphosphoramide (HMPA) in tetrahydrofuran (THF) at low temperature.<sup>11</sup> This observation as well as the presence of 1-methyl-1-silacyclopent-3-ene end groups in poly(1-methyl-1-sila-*cis*-pent-3-ene)<sup>13,14</sup> has been interpreted in terms of the importance of anionic hypervalent siliconate intermediates in these polymerization reactions (see Figure 1).

In this paper, we report that anionic ring-opening polymerization of 1,1-divinyl-1-silacyclopent-3-ene yields poly(1,1-divinyl-1-silacyclopent-3-ene) (polymer) as expected. This carbosilane polymer has a very high degree of unsaturation and is converted on thermal decomposition to a high char yield. However, of greater mechanistic interest, significant amounts of 1,1,6,6-tetravinyl-1,6-disila-3,8-cyclodecadiene (dimer) are isolated along with the polymer. Experiments on the effect of monomer concentration and temperature on the ratio of dimer to polymer provide additional understanding of the mechanism of this reaction. The observation that pure polymer can be equilibrated to a mixture of dimer and polymer under polymerization reaction conditions is particularly significant (see Figure 2).

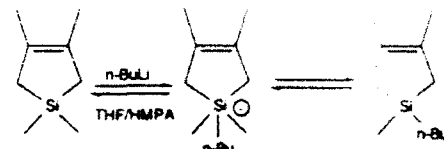


Figure 1. Equilibration of 1-silacyclopent-3-ene via siliconate intermediates.

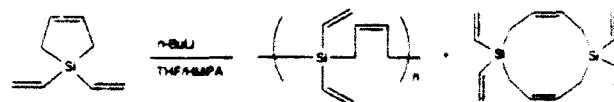
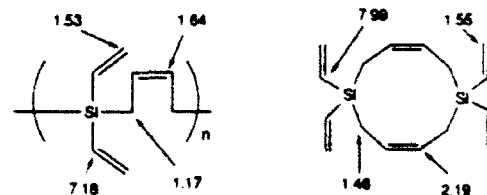


Figure 2. Anionic dimerization-ring-opening polymerization of 1.

Figure 3.  $^{13}\text{C}$  NMR  $T_1$  values in seconds for polymer and dimer.

## Experimental Section

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on a Bruker AM-360 spectrometer operating in the Fourier transform mode.  $^{29}\text{Si}$  NMR spectra were obtained by use of heteronuclear gated decoupling pulse sequence (NOE) with a pulse delay of 20 s.<sup>15</sup> Five percent weight/volume solutions in chloroform-*d* were used to measure  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, whereas 15% solutions were utilized to obtain  $^{29}\text{Si}$  NMR spectra.

The ratio of dimer to polymer was determined by integration of quantitative  $^{13}\text{C}$  NMR spectra.  $^{13}\text{C}$   $T_1$  values for dimer and polymer were determined using the inversion recovery method<sup>16</sup> (Figure 3). Samples of polymer and of mixtures of dimer and polymer dissolved in chloroform-*d* were placed in 5-mm NMR tubes. These solutions were degassed by bubbling UHP argon through them for 2 h. The NMR tubes were then sealed. The spectra were obtained at  $30^{\circ}\text{C}$  on a Bruker SY-270 FT spectrometer using a  $\tau$  pulse of 12.4  $\mu\text{s}$  and a  $\pi/2$  pulse of 6.2  $\mu\text{s}$ . Fifty-six scans were accumulated with relaxation delays of 0.01, 0.1, 0.5, 1.0, 5.0, 10.0, 20.0, 40.0, 80.0, and 120.0 seconds. Analysis of these data gives the  $^{13}\text{C}$   $T_1$  values for both the dimer and the polymer.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</p>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1993	3. REPORT TYPE AND DATES COVERED Journal Article		
4. TITLE AND SUBTITLE Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) M. Theurig and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer Bulletin</u> , 28, 17 (1992).				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS Anionic polymerization Silacyclobutene			15. NUMBER OF PAGES 5	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

## Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene

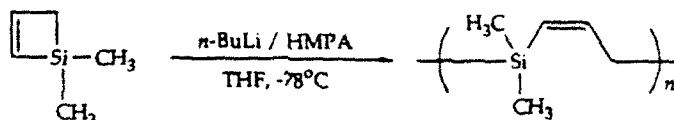
### Characterization of poly(1,1-dimethyl-1-sila-*cis*-but-2-ene)

Marcus Theurig and William P. Weber\*

D. P. and K. B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

#### SUMMARY

Stereoselective anionic ring opening polymerization of 1,1-dimethyl-1-silacyclobutene co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C yields predominantly poly(1,1-dimethyl-1-sila-*cis*-but-2-ene). The polymer has been characterized by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and elemental analysis.



#### EXPERIMENTAL

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). <sup>29</sup>Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume solutions of polymer in chloroform-*d* were used for <sup>1</sup>H NMR spectra, whereas fifteen percent solutions were utilized for <sup>13</sup>C and <sup>29</sup>Si NMR spectra. <sup>13</sup>C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NNOE) with a 20 sec delay was used to acquire <sup>29</sup>Si NMR spectra (1). These were externally referenced to TMS. Chloroform was used as an internal reference for <sup>1</sup>H and <sup>13</sup>C NMR spectra. IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer.

Gel permeation chromatographic analysis of the molecular weight distribution of the polymer was performed on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector and a Model 820 Maxima control system. A Waters 7.8 mm x 30 cm Ultrastaygel linear column packed with less than 10 μm particles of mixed pore size crosslinked styrene divinylbenzene copolymer maintained at 20°C was used for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.8 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: *M<sub>w</sub>* 612,000; 114,000; 47,500; 18,700 and 5,120 whose *M<sub>w</sub>*/*M<sub>n</sub>* are less than 1.09.

Thermogravimetric analysis of the polymer was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cm<sup>3</sup>/min. The temperature program for the analysis was 50°C for 10 min followed by an increase of 4°C/min to 750°C.

Elemental analysis was performed by Galbraith Laboratories, Knoxville TN.

All reactions were carried out under an atmosphere of argon in flame dried glassware. THF was dried by distillation from a deep blue solution of sodium/benzophenone ketyl immediately prior to use. HMPA was distilled from calcium hydride and stored over activated 4 Å molecular sieves.

#### 1,1-Dimethyl-1-silacyclobutene (I)

I was prepared by flash vacuum pyrolysis of diallyldimethylsilane (Aldrich) at 750°C. The <sup>1</sup>H and

\*To whom offprint requests should be sent

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704 0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1993	3. REPORT TYPE AND DATES COVERED Journal Article		
4. TITLE AND SUBTITLE Anionic ring-opening polymerization of 2,3-benzo-1-sila-cyclobutenes. Characterization of poly(2,3-benzo-1-silabutenes)		5. FUNDING NUMBERS N00014-89-J-1961		
6. AUTHOR(S) M. Theurig, S.J. Sargeant, G. Manuel and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Published in Macromolecules, <u>25</u> , 3834 (1992).				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS Anionic ring-opening polymerization 2,3-benzo-1-silacyclobutenes Poly(2,3-benzo-1-silabutenes)			15. NUMBER OF PAGES 4	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

# Anionic Ring-Opening Polymerization of 2,3-Benzo-1-silacyclobutenes. Characterization of Poly(2,3-benzo-1-silabutenes)

Marcus Theurig, Steven J. Sargeant, Georges Manuel, and William P. Weber\*

Katherine B. and Donald P. Loker Hydrocarbon Research Institute Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received January 13, 1992; Revised Manuscript Received April 8, 1992

**ABSTRACT:** Anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III) catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at low temperature ( $-78^{\circ}\text{C}$ ) yields respectively poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR as well as by IR and UV-visible spectroscopy. Their molecular compositions have been determined by elemental analysis. The molecular weight distributions of these polymers have been measured by gel permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures ( $T_g$ ) by differential scanning calorimetry (DSC).

## Introduction

While there has been considerable work done on the ring-opening polymerization of silacyclobutenes, the polymerization of 2,3-benzo-1-silacyclobutene systems has been less thoroughly studied. This paper reports the synthesis and characterization of poly(2,3-benzo-1,1-dimethyl-1-silabutene) (IV), poly(2,3-benzo-1-methyl-1-phenyl-1-silabutene) (V), and poly(2,3-benzo-1,1-diphenyl-1-silabutene) (VI). These polymers were prepared by the anionic ring-opening polymerization of 2,3-benzo-1,1-dimethyl-1-silacyclobutene (I), 2,3-benzo-1-methyl-1-phenyl-1-silacyclobutene (II), and 2,3-benzo-1,1-diphenyl-1-silacyclobutene (III), respectively.

## Experimental Section

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectra were obtained on an IBM-Bruker 270-SY spectrometer operating in the Fourier transform mode.  $^{13}\text{C}$  NMR spectra were run with broad-band proton decoupling. Ten to fifteen percent solutions in chloroform-*d* were used to obtain  $^{13}\text{C}$  and  $^{29}\text{Si}$  NMR spectra. Five percent solutions were used to obtain  $^1\text{H}$  NMR spectra. Chloroform or TMS were utilized as an internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. A heteronuclear gated decoupling pulse sequence (NOE) with a delay of 20 s was used to obtain  $^{29}\text{Si}$  NMR spectra which were externally referenced to TMS.<sup>1</sup>

IR spectra were recorded on a Perkin-Elmer PE-281 spectrometer of neat liquid samples on sodium chloride plates or as potassium bromide pellets for solids. UV spectra were recorded on a Shimadzu UV-260 UV-visible spectrometer. Spectra-quality THF was used to prepare solutions of polymers, and spectra-quality hexane was used to prepare solutions of monomers for UV spectroscopy.

Gel permeation chromatographic (GPC) analysis of the molecular weight distribution of the polymers was performed on a Waters system. This was comprised of a U6K injector, a 510 solvent delivery system, a R401 differential refractometer, and a Maxima 820 data station. A 7.8 mm  $\times$  30 cm Waters Ultrasyl gel linear column packed with  $<10\text{-}\mu\text{m}$  particles of mixed pore size, cross-linked styrene-divinylbenzene copolymer was used for the analysis. The eluant was HPLC-grade THF at a flow rate of 0.8 mL/min. Retention times were calibrated against known monodisperse polystyrene standards  $M_n$  179 000, 110 000, 20 400, and 1350 whose  $M_w/M_n$  are less than 1.09.

Preparative GLPC was carried out on a Gow Mac 550 GC equipped with a 1/4 in.  $\times$  10 ft stainless steel column packed with 10% SE-30 on Chromosorb W NAW 60/80 mesh. The column was deactivated immediately prior to use by injection of 50  $\mu\text{L}$  of hexamethyldisilazane.

Thermogravimetric analysis (TGA) of the polymers was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cm<sup>3</sup>/min. The temperature program for these analyses was 50  $^{\circ}\text{C}$  for 10 min followed by an increase of 5  $^{\circ}\text{C}/\text{min}$  to 100  $^{\circ}\text{C}$ . After 10 min at 100  $^{\circ}\text{C}$  the temperature was increased at a rate of 5  $^{\circ}\text{C}/\text{min}$  to 750  $^{\circ}\text{C}$ . The glass transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-4 system. The initial temperature for the analysis was 30  $^{\circ}\text{C}$ . This was increased at a rate of 20  $^{\circ}\text{C}/\text{min}$  to 200  $^{\circ}\text{C}$ . The melting points of the polymers were also measured on an Electrothermal melting point apparatus and are uncorrected.

High-resolution mass spectra were obtained at the University of California Riverside Mass Spectrometry Facility on a VG-7070 EHF mass spectrometer at an ionizing voltage of 20 eV. Exact masses were determined by peak matching against known masses of perfluorokerosene.

Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN.

Tetrahydrofuran (THF) was distilled immediately prior to use from sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over 4- $\text{\AA}$  molecular sieves. Hexane was distilled from lithium aluminum hydride. *n*-Butyllithium in hexane (2.5 M) and 2-bromobenzyl bromide (Aldrich) were used as received. Dimethyldichlorosilane, methylphenyldichlorosilane, and diphenyldichlorosilane were obtained from H $\ddot{u}$ ls. They were purified by fractional distillation.

All glassware was dried overnight in an oven at 120  $^{\circ}\text{C}$  and was flame dried prior to use. All reactions were conducted under an atmosphere of purified argon.

2,3-Benzo-1,1-dimethyl-1-silacyclobutene (I).<sup>2</sup> I was prepared by the reaction of 2-bromobenzyl bromide and dimethyldichlorosilane with magnesium powder in ether following literature procedures. The product was purified by fractional distillation through a 15-cm vacuum-jacketed Vigreux column. A fraction [bp 106/107  $^{\circ}\text{C}/60\text{ mm}$  (lit.<sup>2</sup> 73  $^{\circ}\text{C}/17\text{ mm}$ )] of 17 g (44% yield) was isolated.  $^1\text{H}$  NMR  $\delta$  0.36 (s, 6 H), 2.06 (s, 2 H), 7.03 (m, 2 H), 7.18 (m, 2 H).  $^{13}\text{C}$  NMR:  $\delta$  -0.45, 20.13, 126.18, 126.91, 130.38, 130.46, 145.94, 150.55.  $^{29}\text{Si}$  NMR:  $\delta$  9.41. IR:  $\nu$  3056, 2960, 2909, 1586, 1450, 1436, 1282, 1247, 1043, 849, 823, 786, 718 cm<sup>-1</sup>. UV:  $\lambda_{\text{max}}$  nm ( $\epsilon$ ) 219 (5300), 262 (1200), 269 (1700), 276 (1550).

2,3-Benzo-1-methyl-1-phenyl-1-silacyclobutene (II). In a 500-mL three-necked round-bottom flask equipped with a reflux condenser, a pressure equalizing addition funnel, and a Teflon-covered magnetic stirring bar was placed magnesium powder (9.7 g, 0.4 mol) and ether (30 mL). A mixture of 2-bromobenzyl bromide (33 g, 0.13 mol) and methylphenyldichlorosilane (26.8 g, 0.4 mol) in ether (150 mL) was placed in the addition funnel

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302 and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article
4. TITLE AND SUBTITLE Synthesis and characterization of poly(1-methyl-1-sila-butane), poly(1-phenyl-1-silabutane) and poly(1-silabutane)			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) C.X. Liao and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer Bulletin</u> , 28, 281 (1992).				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS Poly(1-silabutenes) Reactive Si-H Anionic ring opening polymerization			15. NUMBER OF PAGES 6	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	



## Synthesis and characterization of poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane)

Charles X. Liao and William P. Weber\*

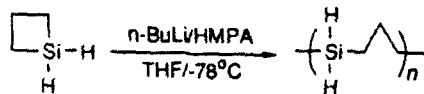
D. P. and K. B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-1661, USA

### Summary:

Anionic ring opening polymerization of 1-methyl-1-silacyclobutane, 1-phenyl-1-silacyclobutane and 1-silacyclobutane co-catalyzed by *n*-butyllithium and hexamethylphosphoramide (HMPA) in THF at -78°C yields poly(1-methyl-1-silabutane), poly(1-phenyl-1-silabutane) and poly(1-silabutane) respectively. These saturated carbosilane polymers possess reactive Si-H bonds. They have been characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR as well as FT-IR and UV spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC), thermal stabilities by thermogravimetric analysis (TGA) and glass transition temperatures (*T*<sub>g</sub>) by differential scanning calorimetry (DSC).

### Introduction

While polymethylhydrosiloxanes are well known commercial products (1), polycarbosilanes which possess reactive Si-H bonds have only recently attracted significant attention. The proposal by Yajima that poly(1-methyl-1-silaethane) (-CH<sub>2</sub>-SiH-CH<sub>2</sub>-)<sub>n</sub> is an intermediate in the pyrolytic conversion of poly(dimethylsilane) fibers into silicon carbide fibers (2,3) stimulated interest in such systems (4,5). Oligo(1-silapropane) has been prepared by hydrosilation polymerization of vinylchlorosilane to yield poly(1,1-dichloro-1-silapropane) followed by reduction of the Si-Cl bonds with lithium aluminum hydride (6,7). Low molecular weight poly(1-methyl-1-sila-*cis*-pent-3-ene) and poly(1-sila-*cis*-pent-3-ene), carbosilane polymers which contain both reactive Si-H and carbon-carbon double bonds have been prepared by anionic ring opening polymerization of 1-methyl-1-silacyclopent-3-ene and 1-silacyclopent-3-ene respectively (8,9).



### Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained on a Bruker AM-360 spectrometer operating in the Fourier Transform mode (FT). <sup>29</sup>Si NMR spectra were recorded on an IBM-Bruker WP-270-SY spectrometer. Five to ten percent weight/volume solutions of polymer in chloroform-*d* were used for <sup>1</sup>H NMR spectra, whereas fifteen to twenty percent solutions were utilized for <sup>13</sup>C and <sup>29</sup>Si NMR spectra. <sup>13</sup>C NMR spectra were run with broad band proton decoupling. A heteronuclear gated decoupling pulse sequence (NOE) with a 20 sec delay was used to acquire <sup>29</sup>Si NMR spectra (10).

\*Corresponding author

# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article	
4. TITLE AND SUBTITLE Synthesis of carbosilane monomers and polymers with mesogenic pendant groups				5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) S.J. Sargeant and W.P. Weber					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217				10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer Preprints</u> , <u>34</u> , 290 (1993).					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments					
14. SUBJECT TERMS carbosilane liquid crystalline materials				15. NUMBER OF PAGES 2	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited		

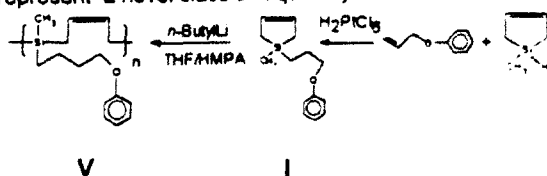
# Synthesis of carbosilane monomers and polymers with mesogenic pendant groups

Steven J. Sargeant and William P. Weber\*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute  
Department of Chemistry, University of Southern California  
Los Angeles, CA 90089-1661

## Introduction

Liquid crystalline (LC) materials demonstrate unusual phase behavior which combine properties of the homogeneous liquid and the ordered crystalline states.<sup>1,2</sup> Polymeric, side chain<sup>3,4</sup> LC materials comprised of a flexible, low  $T_g$ , siloxane backbone in which the silyl centers are substituted with pendant mesogens have been prepared.<sup>5</sup> The low  $T_g$  (-64°C)<sup>6</sup> of poly(1,1-dimethyl-1-sila-cis-pent-3-ene) suggests that materials based on stereoregular unsaturated carbosilane backbones, substituted with pendant aryloxy groups, might exhibit LC behavior at rt. Such materials would represent a novel class of liquid crystalline substances.



## Experimental

THF was distilled from a dark blue solution of sodium benzophenone ketyl under nitrogen. HMPA was distilled over calcium hydride and stored over sieves (4Å) in a syringe sealed container. Chloroplatinic acid (Aldrich) was used without further purification. *n*-Butyllithium (Aldrich) was titrated before use.<sup>7</sup> Allyl phenyl ether (Aldrich) was redistilled before use. 4-Allyloxybiphenyl<sup>8</sup>, 2-allyloxynaphthalene<sup>9</sup>, 1-methyl-1-silacyclopent-3-ene<sup>10</sup>, 1-phenyl-1-silacyclopent-3-ene<sup>11</sup> were prepared by literature procedures.

All reactions were conducted in flame-dried glassware under an atmosphere of UHP argon.

## Monomer synthesis

Monomers were prepared by  $H_2PtCl_6$  catalyzed hydrosilation reactions of 1-methyl-1-silacyclopent-3-ene or 1-phenyl-1-silacyclopent-3-ene and the corresponding allyl aryl ethers, as below.

### 1-Methyl-1-(3'-*p*-biphenoxypropyl)-1-silacyclopent-3-ene(II).

A flask, fitted with a rubber septum, is charged with 4-allyloxybiphenyl and 1-methyl-1-silacyclopent-3-ene.  $H_2PtCl_6$ ,  $1 \times 10^{-3}$  Pt to allyl aryl ether, is added by syringe. The reaction is quenched after 4h via the addition of water/methanol. The organic layer was removed and the aqueous phase was extracted with ether. The combined organic layers were dried over  $CaCl_2$ . The product was purified by flash chromatography on a silica gel column using pentane/chloroform (1:1) as eluant. This removed the Pt complexes. A water white liquid was obtained in 70% yield. Table I, illustrates the monomers which have been prepared.

### Polymer Synthesis by Anionic Ring Opening Polymerization (AROP)

Polymers were synthesized by AROP of the corresponding monomers using *n*-butyllithium and HMPA as co-catalyst in THF solvent, as below.

### Poly-[1-methyl-1-(3'-phenoxypropyl)-1-sila-cis-pent-3-ene](V).

A flask, containing a Teflon covered magnetic stirring bar, was fitted with a rubber septum. THF (10 mL), 100μL of HMPA and 0.50g of (II) were added by syringe. The flask was cooled to -78°C for 15 min, and *n*-butyllithium (120μL) was added via syringe to the stirred solution. The reaction was allowed to proceed for 3h and was quenched via the addition of sat. aq.  $NH_4Cl$ . The organic phase was removed and the aqueous phase was extracted with ether (3x50mL). The combined organic phases were washed with water, dried over anhydrous  $CaCl_2$ , then filtered through a plug of glass wool. The solvents were removed under reduced pressure to yield an opaque, gummy solid. The polymer was twice taken up in a minimum amount of THF, precipitated out of solution with methanol and then centrifuged. Finally, the polymer was dried under vacuum to give 0.43g (80% yield). Table I lists the polymers which were prepared.

Monomer	Polymer	$M_w/M_n$
		241900/149600
		52700/29000
		17200/8460
		29100/16700

Table I, Monomers and polymers prepared for this study.

## Characterization

The structures of the monomers and polymers were confirmed by  $^1H$ ,  $^{13}C$  and  $^{29}Si$  NMR spectroscopy. The molecular weight distribution of the polymers was determined by GPC on a Waters system. TGA was carried out on a Perkin-Elmer TGS-2 instrument. The thermal transitions of the polymers were determined by DSC on a Perkin-Elmer DSC-7.

Polarizing optical microscopy (POM) was done using an Unifon polarizing microscope fitted with a Leitz/Omega hot stage. The polymer films were heated to 80°C and then cooled at 0.5°C/min. Micrographs were obtained at various temperatures at a magnification of 100x with a Polaroid camera attachment.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>1. One reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 1993	3. REPORT TYPE AND DATES COVERED Journal Article		
4. TITLE AND SUBTITLE Synthesis and properties of novel functionally substituted carbosilane polymers.		5. FUNDING NUMBERS N00014-89-J-1961		
6. AUTHOR(S) C.X. Liao and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217		10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES Published in <u>Macromolecules</u> , 26, 563 (1993).				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS functionally substituted carbosilane polymers			15. NUMBER OF PAGES 4	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

# Macromolecules

Volume 26, Number 4

February 15, 1993

© Copyright 1993 by the American Chemical Society

## Synthesis and Properties of Novel Functionally Substituted Carbosilane Polymers

Charles X. Liao and William P. Weber\*

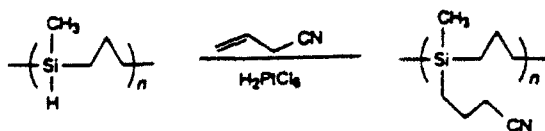
Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661

Received August 11, 1992; Revised Manuscript Received October 20, 1992

**ABSTRACT:** Poly[1-(3'-cyanopropyl)-1-methyl-1-silabutane], poly[1-methyl-1-[3'-(glycidyloxy)propyl]-1-silabutane], poly[1-methyl-1-[3'-(triethoxysilyl)propyl]-1-silabutane], poly[1-methyl-1-(4',7',10'-trioxaundecanyl)-1-silabutane], poly[1-methyl-1-(4',7',10',13'-tetraoxatetradecanyl)-1-silabutane], poly[1-methyl-1-[3'-(phenyloxy)propyl]-1-silabutane], and poly[1-methyl-1-[3'-(pentafluorophenyl)propyl]-1-silabutane] have been prepared by the platinum-catalyzed hydrosilation graft reactions between poly(1-methyl-1-silabutane) and the appropriate functional alkene. These polymers have been characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  (where appropriate), and  $^{29}\text{Si}$  NMR as well as by FT-IR and UV spectroscopy. The molecular weight distributions of these polymers have been determined by gel permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures ( $T_g$ 's) by differential scanning calorimetry.

While there has been considerable work over the last 50 years on silicone polymers,<sup>1,2</sup> there has been much less work on carbosilane polymers. The observation of Yajima that thermal decomposition of poly(methylsilylenemethylene)  $[\text{CH}_3\text{SiHCH}_2]_n$  results in loss of methane and hydrogen and formation of  $\beta$ -silicon carbide<sup>3,4</sup> has stimulated considerable interest in polycarbosilanes.<sup>5</sup>

This paper reports the preparation of saturated carbosilane polymers which have functionally substituted pendant alkyl chains. These have been prepared by the chemical modification, by platinum-catalyzed hydrosilation graft reactions between functional alkenes and the reactive Si-H bonds, of the saturated carbosilane polymer, poly(1-methyl-1-silabutane).<sup>6</sup> There is considerable interest in the chemical modification of intact polymers since this method often permits the synthesis of polymers which cannot be prepared directly.<sup>7,8</sup>



### Background

Numerous types of silicone polymers with functionally substituted pendant alkyl chains have been prepared. The synthesis, chemical properties, and significant applications of these have been reviewed.<sup>9-12</sup> Some of these have

(dimethylsilicones) such as low surface tension, high thermal stability, and low glass transition temperature with properties which are associated with the pendant functional chain. For example, poly[methyl-(3,3,3-trifluoropropyl)siloxane] combines thermal stability and low glass transition temperature with lubricating properties and lack of swelling in hydrocarbon solvents characteristic of perfluoroalkyl polymers.<sup>13,14</sup> Poly[1-(3'-cyanopropyl)-1-methylsiloxane] compounds find utility as thermally stable polar liquid phases for gas-liquid chromatography, while similar chemically bonded siloxane polymers are used in high-pressure liquid chromatography.<sup>15</sup> Poly(3'-aminopropyl)methylsiloxane, poly(3'-(acryloxy)propyl)methylsiloxane, poly(3'-mercaptopropyl)methylsiloxane, poly(3'-cyanopropyl)methylsiloxane, poly(3'-(glycidyloxy)propyl)methylsiloxane are among the silicone polymers with pendant functionally substituted alkyl groups which are commercially available.<sup>11</sup>

Closely related to these are siloxane graft copolymers. These polymeric systems have a siloxane backbone in which some or all of the silyl centers carry functional substituted oligomeric side chains. Important examples of this type of polymer are polysiloxanes substituted with hydrophilic nonionic oligo(oxyethylene) pendant groups. These find commercial application as surfactants<sup>16</sup> and are of scientific interest due to their ability to complex lithium cations to form solvent-free polymer electrolytes which have reasonable ionic conductivities.<sup>17-20</sup> These have been prepared by the platinum-catalyzed hydrosi-

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
Public report to Government for collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 1993	3. REPORT TYPE AND DATES COVERED Journal Article		
4. TITLE AND SUBTITLE Synthesis, characterization and platinum catalyzed cross-linking of copoly(1-silacyclobut-1-ylidene-1,4-phenylene).			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) C.X. Liao, M.W. Chen and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer Preprints</u> , <u>34</u> , 230 (1993).				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS carbosilane thermosets crosslinking silacyclobutane			15. NUMBER OF PAGES 2	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

# SYNTHESIS, CHARACTERIZATION and PLATINUM CATALYZED CROSSLINKING of COPOLY(1-SILA-CYCLOBUT-1-YLIDENE-1,4-PHENYLENE). PROPERTIES of AROMATIC CARBOSILANE THERMOSET

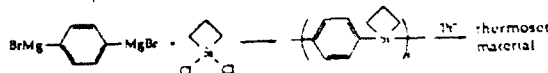
Charles X. Liao, Min Wei Chen and William P. Weber\*  
D. P. and K. B. Loker Hydrocarbon Research Institute, Dept. of Chem., U. of Southern California, Los Angeles, CA 90089-1661

## ABSTRACT:

Low molecular weight copoly(1-silacyclobut-1-ylidene-1,4-phenylene) (I) has been prepared by the reaction of 1,1-dichloro-1-silacyclobutane (II) with the di-Grignard reagent prepared from *p*-dibromobenzene. I has been characterized by <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR as well as FT-IR and UV spectroscopy. Its molecular weight distribution has been determined by GPC, and its thermal stability by TGA in both nitrogen and air. Thermal degradation of I in nitrogen gives high (60-62%) char yield. T<sub>g</sub> of I has been measured by DSC. Platinum catalyzed ring opening of the strained silacyclobutane rings crosslinks I. The bending modulus log E', tan δ and T<sub>g</sub> of this thermoset material has been determined by DMTA. Electrical properties: dielectric constant and dissipation factor are reported.

## Introduction:

1,1-Disubstituted-1-silacyclobutanes undergo platinum catalyzed 1,2 thermal 3,4 as well as anionic ring opening polymerization 5,8. Ring opening of silacyclobutane and 1,3-disilacyclobutane units has been utilized to crosslink polysilacyclobutasilazanes 9-12. Crosslinking is a essential requirement for the high yield conversion of organometallic polymers to ceramic materials 13,14. Silacyclobutanes have not been previously used to crosslink polycarbosilanes. Condensation polymerization of aromatic di-Grignard reagent prepared from *p*-dibromobenzene with II leads to low molecular weight I. This viscous liquid has a low T<sub>g</sub>. Platinum catalyzed crosslinking of I yields a thermoset material which has a T<sub>g</sub> above 170°C, high bending modulus, low dielectric constant and dissipation factor.



## Experimental:

<sup>1</sup>H and <sup>13</sup>C NMR spectra were run on a Bruker AM-250 spectrometer operating in the FT mode. <sup>29</sup>Si NMR spectra was recorded on a Bruker 270-ST spectrometer. <sup>13</sup>C NMR spectra were run with broad band proton decoupling. <sup>29</sup>Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a pulse delay of 15-20 s. <sup>15</sup>N and <sup>29</sup>Si NMR spectra were obtained in 15% solution of chloroform-*d*. <sup>1</sup>H NMR spectra were obtained in 5% solution of chloroform-*d*. IR spectra was recorded on an IBM FT-IR/30S DTGS/CSI spectrometer of neat films on sodium chloride plates. UV spectra of ethyl ether solutions were recorded on a Shimadzu UV-260 spectrometer.

The molecular weight distribution of this polymer was determined by GPC on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractometer and a Maxima 820 control system. A Waters 7.8 mm x 30 cm Ultrastaygel linear column packed with < 10 μm particles of mixed pore size crosslinked styrene-divinylbenzene copolymer was utilized for the analysis. The column was maintained at rt. The eluting solvent was HPLC grade THF at a flow rate 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: 47,500, 18,700, 5,120 and 2,200 whose M<sub>w</sub>/M<sub>n</sub> values are < 1.09.

TGA was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 cc/min. The temperature program for the analysis was 50 °C for 2 min. The temperature was then increased at a rate of 50°C/min to 750 or 800°C. T<sub>g</sub> of I was determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting point of indium (156 °C) and spectral grade *n*-hexane (-95 °C) were utilized to calibrate the DSC. The temperature scans were begun at -100 °C for 5 min. The temperature was then increased at a rate of 20 °C/min to 150 °C. DMTA of cured materials was performed on a Polymer Laboratories DMTA Mk II. A standard single cantilever bending head (-150-300°C) was used. The analysis was carried out at frequency of 0.1, 1 and 5 Hz at a strain level of 2. The temperature was increased at 40°C/min. Dielectric constant and dissipation factor were determined on a DuPont DEA-2970 Dielectric Analyzer.

THF was distilled from a deep blue solution of sodium/benzophenone ketyl prior to use. All reactions were conducted in dried glassware under argon. Magnesium powder, 1,4-dibromobenzene and 1,3-divinyl-tetramethyldisiloxane platinum complex (2-3% Pt) in xylene (Pt complex) (Huls) were used. 1,1-Dichloro-1-silacyclobutane (II) was prepared by Grignard cyclization of 3-chloropropyltrichlorosilane with magnesium powder in ethyl ether 16-18.

## Copoly(1-silacyclobut-1-ylidene-1,4-phenylene) (I)

In a 500 mL three necked rb flask equipped with a rubber septum, an efficient reflux condenser, a pressure equalizing addition funnel and a Teflon covered magnetic stirring bar was placed magnesium powder (3.0 g, 124 mmol) and 1,4-di-bromobenzene (13.4 g, 56.8 mmol) in THF (200 mL). The reaction mixture was stirred at rt until the magnesium had disappeared (11.3 g, 56.7 mmol) in THF (20 mL) was slowly added to the reaction mixture. After completion of the addition the mixture was stirred for 4 h at reflux. Water (20 mL) was added. The organic layer was separated and aqueous layer was washed with 2 x 30 mL ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered and the volatile solvents were removed by evaporation under reduced pressure. The residue was dissolved in a minimum amount of THF and the polymer was precipitated from ether. This process was repeated twice. The polymer was dried under vacuum. This way 7.5 g, 90 % yield of the polymer. T<sub>g</sub> = 280°C. M<sub>w</sub>/M<sub>n</sub> = 2650/1430 was obtained. <sup>1</sup>H NMR δ: 1.43-1.54 (m, 4H); 2.00-2.30 (m, 2H); 7.32-7.71 (m, 4H); <sup>13</sup>C NMR δ: 13.76, 13.93, 18.27, 18.32, 18.36, 18.42, 19.74, 19.94, 127.96, 131.19, 131.28, 132.54, 133.79, 133.86, 134.45, 135.66, 136.03; <sup>29</sup>Si NMR δ: 6.72, 6.96, 7.20; IR ν: 3363, 3049, 2969, 2926, 2871, 1557, 1468, 1440, 1422, 1403, 1385, 1360, 1232, 1172, 1129, 1061, 1016, 961, 905, 881, 832, 784, 719, 690, 630 cm<sup>-1</sup>. UV λ<sub>max</sub> (nm): 240.2, 176.0, 266.2, 656.

## Crosslinking of I

In a 100 ml rb flask, I (6.0 g) and Pt complex (150 μL) were dissolved in THF (20 mL). The solvent was removed under reduced pressure at a temperature < 70°C. The sample was dried at 40°C for 12 h under vacuum in a mold. It was cured at 150°C in vacuum drying oven for 1 h, and then at 200°C for another 1 h (A-I). Other samples of I were cured at 150 °C for 3 h, and then at 200°C for 5 h (B-I). **Results and Discussion**

I has been prepared by the reaction of the di-Grignard reagent prepared from 1,4-dibromobenzene with II in THF. End groups: phenyl, *p*-bromophenyl, or silanol are important due to the low molecular weights of I (M<sub>w</sub>/M<sub>n</sub> = 2,600/1,400). These leads to extra signals in the <sup>13</sup>C NMR spectra of I. Bands at 3363, 1120 and 1128 cm<sup>-1</sup> assigned to SiOH groups have been detected in the FT-IR spectra of I.

The thermal stability of I was determined by TGA in nitrogen. I is stable to 60°C. Between 60 and 250°C, a 9% weight loss was observed. Little further weight loss occurs between 250 and 460°C. Above 460°C rapid weight loss occurs. By 620°C, 31% percent of the original weight of the sample was been lost. No further weight loss was detected on heating to 800°C. A 60% char yield was obtained (Figure 1). This high char yield probably results from thermal crosslinking due to opening of the silacyclobutane rings of I 3,4.

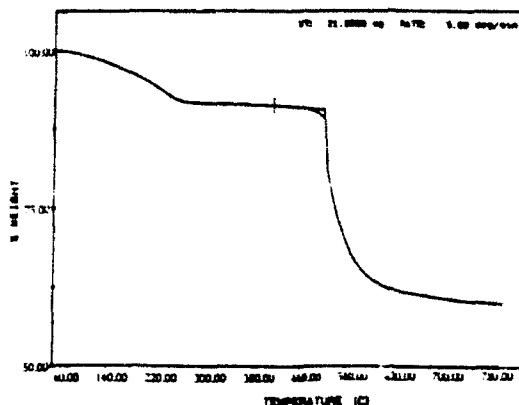


Figure 1. TGA of polymer I in nitrogen.

The thermal stability of Pt cured I was also determined by TGA in nitrogen. The major difference between the Pt cured and non-cured sample of I is that the initial weight loss is eliminated. This initial weight loss is probably due to low molecular weight oligomers. Weight loss at high temperature (>200°C) is similar for both cured and Pt cured samples. This suggests that the degree of crosslinking of achieved by thermal and Pt crosslinking may be similar.

The thermal stability of a Pt cured I was also measured in the air. It was thermally stable to 250°C. Between 250 and 365°C, a 35% weight loss is observed. Between 365 and 500°C, an additional 15% weight loss is detected. Above 500°C, a second rapid weight loss occurs. No further weight loss is detected above 620°C (Figure 2).

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, U.S. Office of Management and Budget, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE		3. REPORT TYPE AND DATES COVERED Journal Article
4. TITLE AND SUBTITLE Anionic polymerizations of trimethylvinylsilane and phenyl- dimethylvinylsilane towards the synthesis of well-defined polyfluorodimethylvinylsilane & polyvinylalcohol.			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) Y. Gao, W.P. Weber, S. Prakash, G.A. Olah and T.E. Hogen-Esch				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  Published in <u>Polymer Preprints</u> , <u>34</u> , 548 (1993).				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  See attachments				
14. SUBJECT TERMS anionic polymerization chemical modification of polymers			15. NUMBER OF PAGES 2	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	



# ANIONIC POLYMERIZATIONS OF TRIMETHYLVINYL-SILANE AND PHENYLDIMETHYLVINYL-SILANE TOWARDS THE SYNTHESIS OF WELL-DEFINED POLYFLUORO-DIMETHYLVINYL-SILANE AND POLYVINYLALCOHOL

Yaodong Gan, William P. Weber, Surya Prakash,

George A. Olah and Théo E. Hogen-Esch

Loker Hydrocarbon Institute

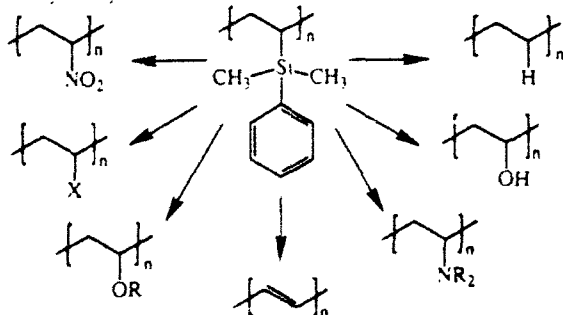
Department of Chemistry

University of Southern California

Los Angeles, CA 90089

## Introduction

Over the last decade, polytrimethylvinylsilane (PTMVS) and polyphenyldimethylvinylsilane (PPDMVS) and their copolymers and polymer blends have been widely applied and studied as materials for gas-separation membranes (1-3), optical fibers (4), contact lenses (5,6), waterproofing fabrics (7), optical disks (8), semiconductor devices (9), etc. However, reactions of PTMVS and PPDMVS to give other potentially useful polymers have not been explored. Thus, narrow molecular weight distribution (MWD) PTMVS and PPDMVS might be useful as intermediates in the synthesis of monodisperse polyethylene, polyvinylalcohol, polyacetylene, polyvinylhalide, polynitroethylene and polyvinylamine (Scheme 1). Such polymers can not readily be synthesized.



Scheme 1

## Anionic Polymerization of Trimethylvinylsilane (TMVS) and Phenyldimethylvinylsilane (PDMVS)

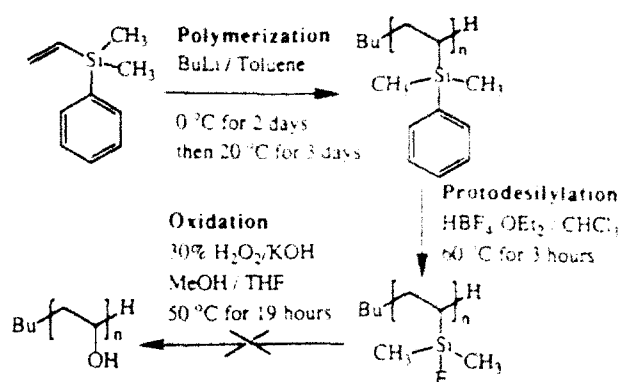
Silicon stabilizes  $\alpha$ -carbanions due to its vacant d orbitals (10). Vinylsilanes such as TMVS and PDMVS are therefore good candidates for "living" anionic polymerizations. Anionic polymerization of TMVS and PDMVS was first reported by N. S. Nametkin et al. in 1965 (11). They synthesized oligomers (12), homopolymers (11), block- (13) and graft- copolymers (14) under various conditions (11,13,15,16). They also reported the occurrence of termination reactions resulting from hydride elimination (17,18). Later studies by Rickle confirmed such side reactions and their effects on MWD and yield (19,20). He also found that such side reactions were enhanced by the addition of ethers (20). We now wish to report the synthesis of monodisperse polyvinylsilanes by anionic polymerization and their attempted transformation into other polymers.

## Synthesis of monodisperse polyfluorodimethylvinylsilane (PPDMVS) and polyvinylalcohol (PVA)

Protodesilylation and oxidation of various of organosilicon compounds had been recently demonstrated by Tamao (21,22,23), Fleming (24,25) and Nishiyama (26), but none of these involved polymers. We now wish to report on such transformations for PPDMVS employing similar reaction conditions (Scheme 2).

## Experimental

**Materials:** TMVS was purchased from Huls America Inc. PDMVS was synthesized by adding vinylchlorosilane



Scheme 2

(Huls America Inc.) to a phenylmagnesium bromide/THF solution at  $-20^{\circ}\text{C}$  followed by reflux for 2 hours. Over 70% isolated yield of product was obtained. Both TMVS and PDMVS were distilled from CaH<sub>2</sub> twice under vacuum prior to use. Toluene was purified by stirring over fresh K-Na alloy under vacuum overnight. Tetrafluoroboric acid-diethyl ether complex (85%) was purchased from Aldrich Chemical Co. PPDMVS was purified by reprecipitation in THF using MeOH as the non-solvent.

**Polymerizations:** Anionic polymerization was carried out by initiation of purified TMVS and PDMVS with *n*-, *sec*-, or *tert*-butyllithium in toluene at various temperatures (in the  $-70^{\circ}\text{C}$  to  $20^{\circ}\text{C}$  range especially at the lower temperatures). The reaction usually took 12 hours to several days. The colorless solution was finally reacted with methanol and precipitated in cold MeOH. Polystyrene-*b*-TMVS block copolymers were synthesized via the same procedure.

**Protodesilylation Reactions:** The reaction of PPDMVS with HBF<sub>4</sub>·Et<sub>2</sub>O was carried out in a polypropylene vessel. Low MW of PPDMVS (DP=46) were first tried in order to obtain more complete substitution. The purified PPDMVS was dissolved in chloroform, and HBF<sub>4</sub>·Et<sub>2</sub>O was then introduced under argon. The reaction mixture was stirred at  $60^{\circ}\text{C}$  for 3 hours. During this protodesilylation process, the reaction temperature was carefully monitored in order to prevent boiling of the solvent and swelling of the plastic vessel. After evaporation of the volatile materials, the resulting fluorosilane polymer was characterized by <sup>1</sup>H and <sup>19</sup>F NMR and by SEC.

**Oxidation Reactions:** The PDMVS obtained was dissolved in THF and transferred to a glass flask. A 15% KOH solution in MeOH was introduced into the reaction vessel followed by the dropwise addition of 30% H<sub>2</sub>O<sub>2</sub> aqueous solution. The reaction mixture was refluxed ( $50^{\circ}\text{C}$ ) for 4-19 hours. The resulting polymer was not water-soluble indicating that conversion was incomplete. We then tried to use dioxane instead of THF/MeOH solvents following the same reaction procedure. We also tried replacing H<sub>2</sub>O<sub>2</sub> by three equivalents of *m*-chloroperbenzoic acid (MCPBA) with an excess of triethylamine in THF/MeOH and refluxing for 19 hours.

## Results and Discussion

In the synthesis of PTMVS and polystyrene-*b*-TMVS, best results were obtained at  $-20^{\circ}\text{C}$  in toluene for four days. In the case of PDMVS, we carried out polymerization reaction in toluene at  $0^{\circ}\text{C}$  for 2 days and then raised temperature to  $20^{\circ}\text{C}$  for another 3 days, which always gave the best results. The MW of the polymers we obtained ranged from 3,000 to 23,000 with MWD's around 1.1 and yields of 90-95%. The long reaction

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, U.S. Government Printing Office, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1993		3. REPORT TYPE AND DATES COVERED Journal Article
4. TITLE AND SUBTITLE Bulk anionic ring opening polymerization of silacyclo- pent-3-enes			5. FUNDING NUMBERS N00014-89-J-1961	
6. AUTHOR(S) S.J. Sargeant, M.A. Tapsak and W.P. Weber				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Loker Hydrocarbon Research Institute University of Southern California Los Angeles, CA 90089-1062			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Avenue Arlington, VA 22217			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Published in <u>Polymer Bulletin</u> , 30, 127 (1993).				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) See attachments				
14. SUBJECT TERMS anionic ring opening polymerization silacyclopent-3-enes			15. NUMBER OF PAGES 5	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

## Bulk anionic ring opening polymerization of silacyclopent-3-enes

Steven J. Sargeant, Mark A. Tapsak, and William P. Weber\*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute, Chemistry Department,  
University of Southern California, Los Angeles, CA 90089-1661 USA

### Summary

Poly[1,1-diphenyl-1-sila-*cis*-pent-3-ene](I), poly[1,1-dimethyl-1-sila-*cis*-pent-3-ene](II), poly[1-methyl-1-phenyl-1-sila-*cis*-pent-3-ene](III), poly[1-methyl-sila-*cis*-pent-3-ene](IV), and poly[1-phenyl-1-sila-*cis*-pent-3-ene](V) were prepared by bulk anionic ring opening polymerization of the corresponding 1-silacyclopent-3-enes, at room temperature by use *n*-butyllithium or *t*-butyllithium and HMPA as co-catalysts. No solvent (THF or diethyl ether) was utilized.

### Introduction

Stereoregular poly[1-sila-*cis*-pent-3-enes] have previously been prepared by the anionic ring opening polymerization of the corresponding 1-silacyclopent-3-enes in THF (1-4) or diethyl ether (5) at low temperature (-40 to -78°C) by use of alkylolithium and HMPA, TMEDA or DMPU as co-catalysts. While these reactions proceed readily in high yield, experimentally they are difficult to carry out on preparative scale. Specifically, the ether solvents must be rigorously purified by distillation from sodium benzophenone ketyl under inert atmosphere immediately prior to use. The ever present possibility of the formation of hydroperoxide impurities in ether solvents is an additional concern. Maintenance of low reaction temperature requires specialized cooling equipment. In this paper, we report a simplified stereoregular high yield polymerization of 1-silacyclopent-3-enes to the corresponding poly[1-sila-*cis*-pent-3-enes].

### Experimental

#### *Monomers and reagents*

Monomers were prepared by published procedures (1-5).

HMPA was redistilled and stored over activated molecular sieves (4Å) in a Mininert syringe valve container. *n*-Butyllithium, 2.5M in hexane, and *t*-butyllithium, 2.0M in hexanes, were purchased from Aldrich and were titrated before use (6).

\*Corresponding author